

Equilibrium Constants

Consider $aA + bB \rightleftharpoons yY + zZ$ $\Delta v = y + z - a - b$

Thermodynamic Equilibrium Constant

$$K^\circ = \prod_i \left(\frac{p_i}{P^\circ} \right)_{\text{eq}}^{\nu_i} = \frac{\left(p_Y / P^\circ \right)_{\text{eq}}^y \left(p_Z / P^\circ \right)_{\text{eq}}^z}{\left(p_A / P^\circ \right)_{\text{eq}}^a \left(p_B / P^\circ \right)_{\text{eq}}^b}$$

Some books still refer to the pressure equilibrium constant

$$K_p = \frac{\left(p_Y \right)_{\text{eq}}^y \left(p_Z \right)_{\text{eq}}^z}{\left(p_A \right)_{\text{eq}}^a \left(p_B \right)_{\text{eq}}^b} \quad \text{which in general has pressure units}$$

The equilibrium constant can also be expressed in mole fractions:

$$K^\circ = \frac{\left(\chi_Y P_{\text{tot}} / P^\circ \right)_{\text{eq}}^y \left(\chi_Z P_{\text{tot}} / P^\circ \right)_{\text{eq}}^z}{\left(\chi_A P_{\text{tot}} / P^\circ \right)_{\text{eq}}^a \left(\chi_B P_{\text{tot}} / P^\circ \right)_{\text{eq}}^b} = K_x \left(\frac{P_{\text{tot}}}{P^\circ} \right)^{\Delta v}$$

and in concentrations:

$$p_i = n_i RT / V = c_i RT$$

$$K^\circ = \prod_i \left(\frac{p_i}{P^\circ} \right)_{\text{eq}}^{\nu_i} = \prod_i \left(\frac{c_i RT}{P^\circ} \right)_{\text{eq}}^{\nu_i} = \left(\frac{c^\circ RT}{P^\circ} \right)^{\sum \nu} K_c$$

where

$$K_c = \frac{\left([Y] / c^\circ \right)_{\text{eq}}^y \left([Z] / c^\circ \right)_{\text{eq}}^z}{\left([A] / c^\circ \right)_{\text{eq}}^a \left([B] / c^\circ \right)_{\text{eq}}^b}$$

for this example

Equilibrium Calculations

	2 NO	+	Cl ₂	→	2NOCl
stoichiometry	-2		-1		+2
initial moles	2		1		0
during reaction	2(1-a)		1-a		2a
mole fraction	$\frac{2(1-a)}{3-a}$		$\frac{1-a}{3-a}$		$\frac{2a}{3-a}$
partial pressure	$\frac{2(1-a)}{3-a} \frac{P}{P^\circ}$		$\frac{1-a}{3-a} \frac{P}{P^\circ}$		$\frac{2a}{3-a} \frac{P}{P^\circ}$

$$K_x = \frac{\left\{ \frac{2a}{3-a} \right\}^2}{\left\{ \frac{2(1-a)}{3-a} \right\}^2 \left\{ \frac{1-a}{3-a} \right\}} = \frac{a^2(3-a)}{(1-a)^3}$$

$$K^\circ = K_x \left(\frac{P^\circ}{P} \right)$$

The value of a at equilibrium (and thus the equilibrium composition of the reaction mixture) depends on pressure.

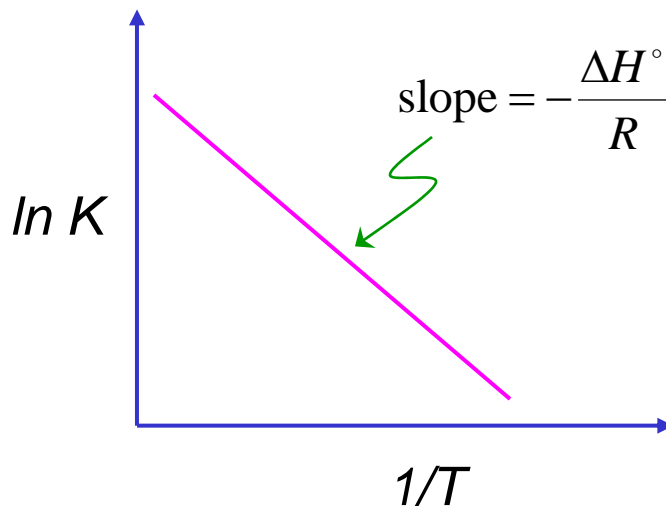
Temperature Dependence of K_P

Gibbs-Helmholtz $\left(\frac{\partial(\Delta G/T)}{\partial T}\right)_P = -\frac{\Delta H}{T^2}$

substitute $\Delta G_{\text{rxn}}^\circ = -RT \ln K$

van't Hoff Equation $\left(\frac{\partial(\ln K)}{\partial T}\right)_P = \frac{\Delta_r H^\circ}{RT^2}$

or $\left(\frac{\partial(\ln K)}{\partial(1/T)}\right)_P = -\frac{\Delta_r H^\circ}{R}$



Exothermic reactions: $\Delta H < 0$ so K falls with increasing T .

Endothermic reactions: $\Delta H > 0$ so K rises with increasing T .

Integrating, $\ln \left\{ \frac{K(T_2)}{K(T_1)} \right\} = -\frac{\Delta H^\circ}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$

or from $\Delta G_{\text{rxn}}^\circ = -RT \ln K$ $\ln K(T) = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$

Pressure Dependence of Equilibrium

Since $K^\circ = \exp(-\Delta G^\circ / RT)$, $\left(\frac{\partial K^\circ}{\partial P}\right)_T = 0$

But, $K_x = K^\circ (P / P^\circ)^{-\Delta v}$

$$\begin{aligned}\ln K_x &= \ln K^\circ - \Delta v \ln(P / P^\circ) \\ &= \ln K^\circ - \Delta v \ln P + \Delta v \ln P^\circ\end{aligned}$$

$$\left(\frac{\partial \ln K_x}{\partial \ln P}\right)_T = -\Delta v$$

$$\left(\frac{\partial \ln K_x}{\partial P}\right)_T = -\frac{\Delta v}{P} = -\frac{\Delta V}{RT} \quad \text{ideal gas}$$

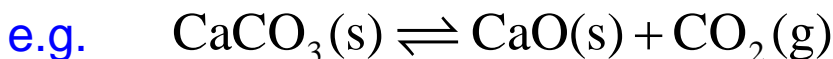
Although the thermodynamic equilibrium constant does not depend on pressure, the K for mole fraction does if $\Delta v \neq 0$

The equilibrium composition depends on pressure if $\Delta v \neq 0$

Le Chatelier's Principle

A system at equilibrium, when subjected to a perturbation, responds in a way that tends to minimize the effect.

Equilibria Involving Condensed Matter



$$\left(\frac{\partial G}{\partial \xi} \right)_{T,P} = -\mu(\text{CaCO}_3) + \mu(\text{CaO}) + \mu(\text{CO}_2)$$

where $\mu(\text{CO}_2) = \mu^\circ(\text{CO}_2) + RT \ln(p_{\text{CO}_2} / P^\circ)$

but $\mu(\text{CaCO}_3) \approx \mu^\circ(\text{CaCO}_3)$

$$\mu(\text{CaO}) \approx \mu^\circ(\text{CaO})$$

At equilibrium, $\left(\frac{\partial G}{\partial \xi} \right)_{T,P} = 0$

$$\Rightarrow \Delta \bar{G}^\circ + RT \ln(p_{\text{CO}_2}^{\text{eq}} / P^\circ) = 0$$

$$K^\circ = (p_{\text{CO}_2}^{\text{eq}} / P^\circ)$$

K depends only on the partial pressures of the gaseous reaction components.

A special case is the evaporation of a liquid: $\text{L}(\text{l}) \rightleftharpoons \text{G}(\text{g})$

$$K^\circ = (p_{\text{G}}^{\text{eq}} / P^\circ)$$

$$\frac{\partial \ln K^\circ}{\partial T} = \frac{\partial \ln P}{\partial T} = \frac{\Delta H_{\text{vap}}^\circ}{RT^2}$$

Phase Equilibria

Consider a closed system of a single component.

The **chemical potential** determines which phase is stable at a particular T and P . μ tends to a minimum.

At the melting point T_m , $\mu(s) = \mu(l)$

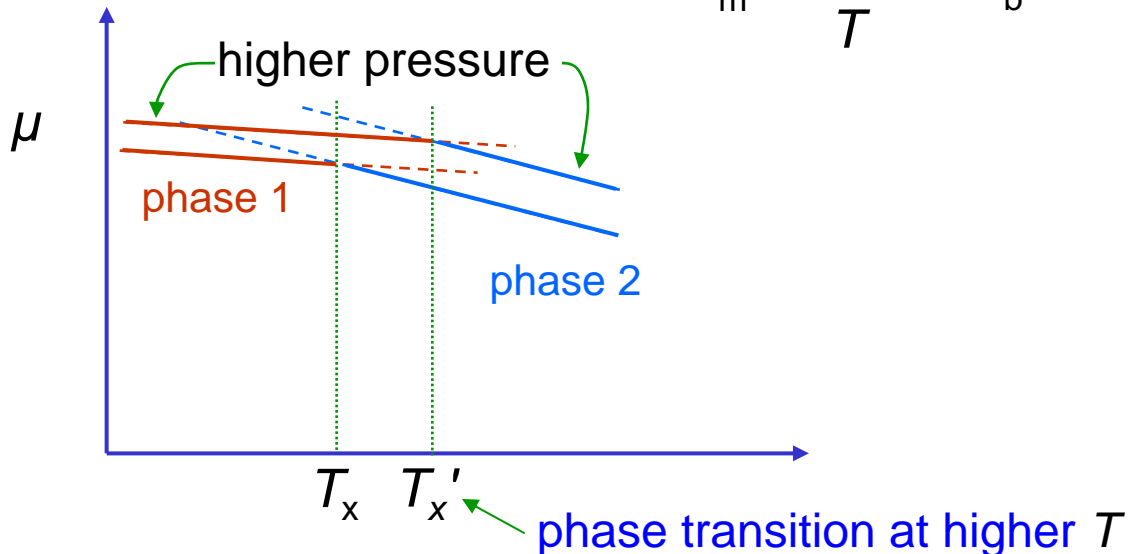
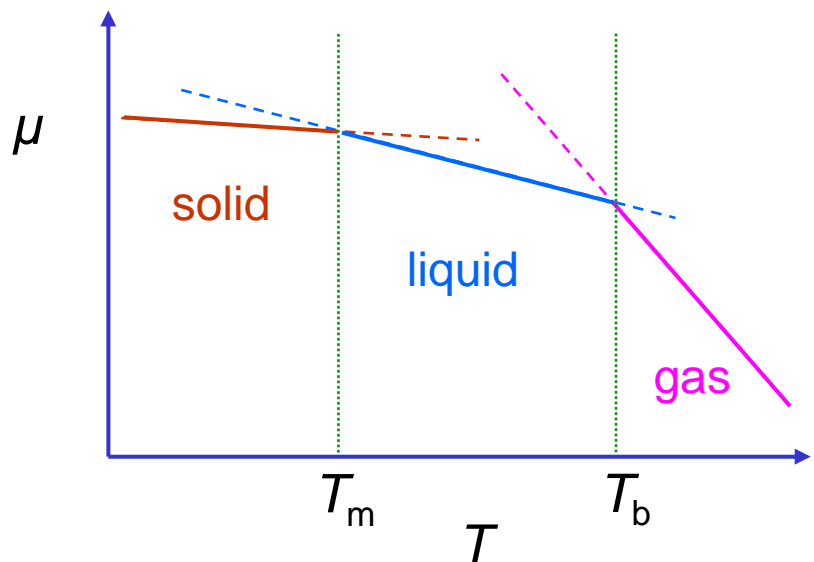
At the boiling point T_b , $\mu(l) = \mu(g)$

These points depend on temperature and pressure.

$$dG = VdP - SdT$$

$$\left(\frac{\partial\mu}{\partial T}\right)_P = -\bar{S}$$

$$\left(\frac{\partial\mu}{\partial P}\right)_T = \bar{V}$$



The Clapeyron Equation

Consider two phases α and β in equilibrium:

$$\mu(\alpha, T, P) = \mu(\beta, T, P)$$

If small changes in T and P are made such that α and β are still in equilibrium:

$$d\mu(\alpha, T, P) = d\mu(\beta, T, P)$$

$$-\bar{S}(\alpha)dT + \bar{V}(\alpha)dP = -\bar{S}(\beta)dT + \bar{V}(\beta)dP$$

$$[\bar{V}(\alpha) - \bar{V}(\beta)]dP = [\bar{S}(\alpha) - \bar{S}(\beta)]dT$$

$$\frac{dP}{dT} = \frac{\Delta\bar{S}}{\Delta\bar{V}} = \frac{\Delta\bar{H}}{T\Delta\bar{V}}$$

Melting

$$\frac{dP}{dT} = \frac{\Delta\bar{H}_m}{T_m \Delta\bar{V}_m}$$

Integrating,

$$P_2 - P_1 = \frac{\Delta\bar{H}_m}{\Delta\bar{V}_m} \ln \left\{ \frac{T_m(P_2)}{T_m(P_1)} \right\}$$
$$\approx \frac{\Delta\bar{H}_m}{\Delta\bar{V}_m} \frac{\Delta T}{T_m}$$

$$\Delta\bar{H}_m > 0 \quad \text{and usually} \quad \Delta\bar{V}_m > 0$$

$\Rightarrow T_m$ increases with pressure *not for water!*

The Clausius-Clapeyron Equation

Vaporization

$$\frac{dP}{dT} = \frac{\Delta\bar{H}_{\text{vap}}}{T\Delta\bar{V}_{\text{vap}}} \approx \frac{\Delta\bar{H}_{\text{vap}}}{T\bar{V}(g)}$$

Assuming the vapour is an ideal gas, $\bar{V}(g) = RT / P$

$$\frac{d \ln P}{dT} = \frac{\Delta\bar{H}_{\text{vap}}}{RT^2}$$

Integrating,

$$\ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta\bar{H}_{\text{vap}}}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$

The normal boiling point is the temperature at which the vapour pressure becomes standard, i.e. 1 bar.

Sublimation solid \leftrightarrow gas

The liquid is not stable at any temperature.

Triple Point: solid, liquid and gas are all in equilibrium

This happens at the pressure where the sublimation temperature and the boiling temperature coincide.

At the triple point,

vapour pressure of liquid = vapour pressure of solid

T_{triple} and P_{triple} are fixed.

The Phase Rule

How many intensive variables are needed to describe fully a system of C components and P phases?

- Two for temperature and pressure.
- How many for the composition of each phase?

Take mole fractions of each component in each phase

$$\Rightarrow P \times (C - 1) \quad \text{C-1 because for each phase } \sum \chi_i = 1$$

but since the phases are in equilibrium,

$$\mu(\text{phase 1}) = \mu(\text{phase 2}) = \dots$$

$(P - 1)C$ variables are redundant

$$\therefore \text{Number of independent concentration variables} = P(C - 1) - (P - 1)C = C - P$$

$$\therefore \text{Total number of variables (degrees of freedom)} \quad F = C - P + 2$$

Phase: A state of matter that is uniform throughout, in both chemical composition and physical state.

Component: The number of components is the minimum number of independent species necessary to define the composition of all phases in the system.

Reactions and phase equilibria must be taken into account.

Phase Diagrams of Pure Materials

$$F = C - P + 2 \quad \text{with } C = 1 \Rightarrow F = 3 - P$$

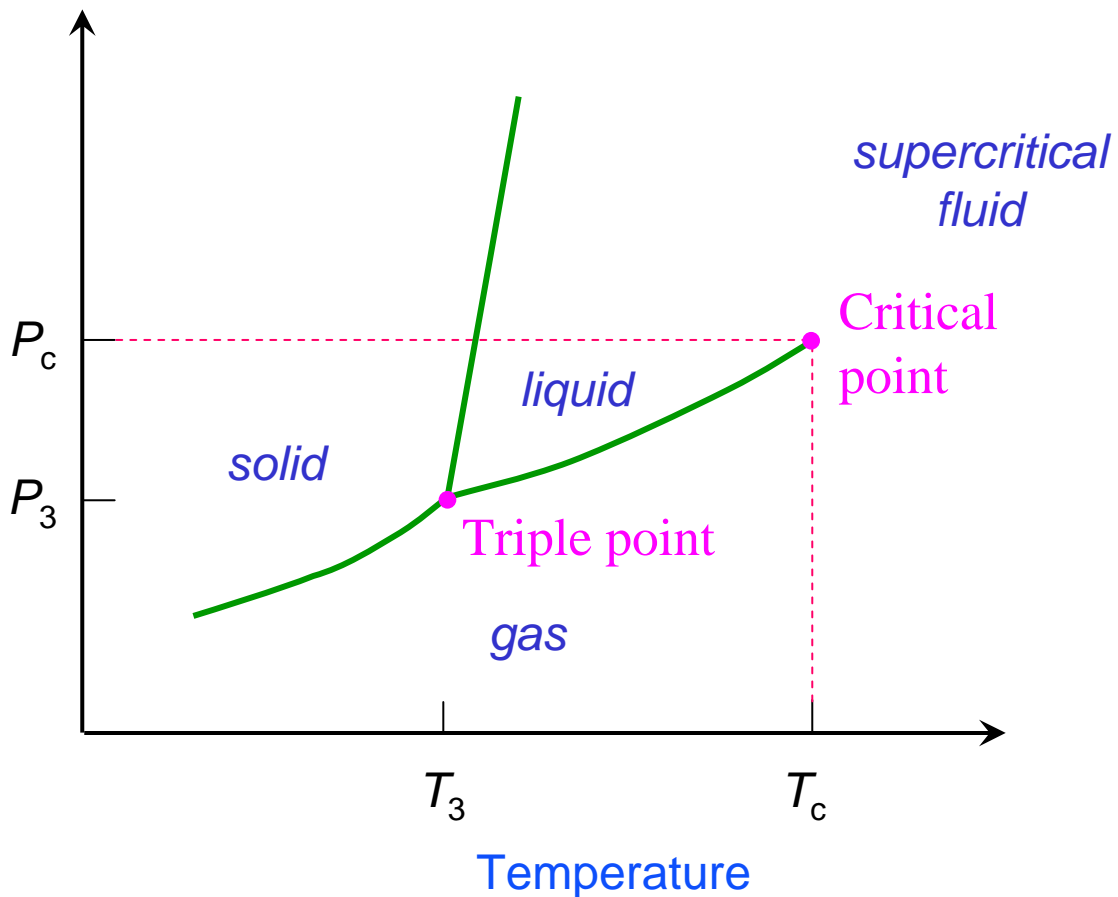
For single phase regions there are 2 degrees of freedom.

For phase boundaries there is 1 degree of freedom.

At the triple point there is no freedom.

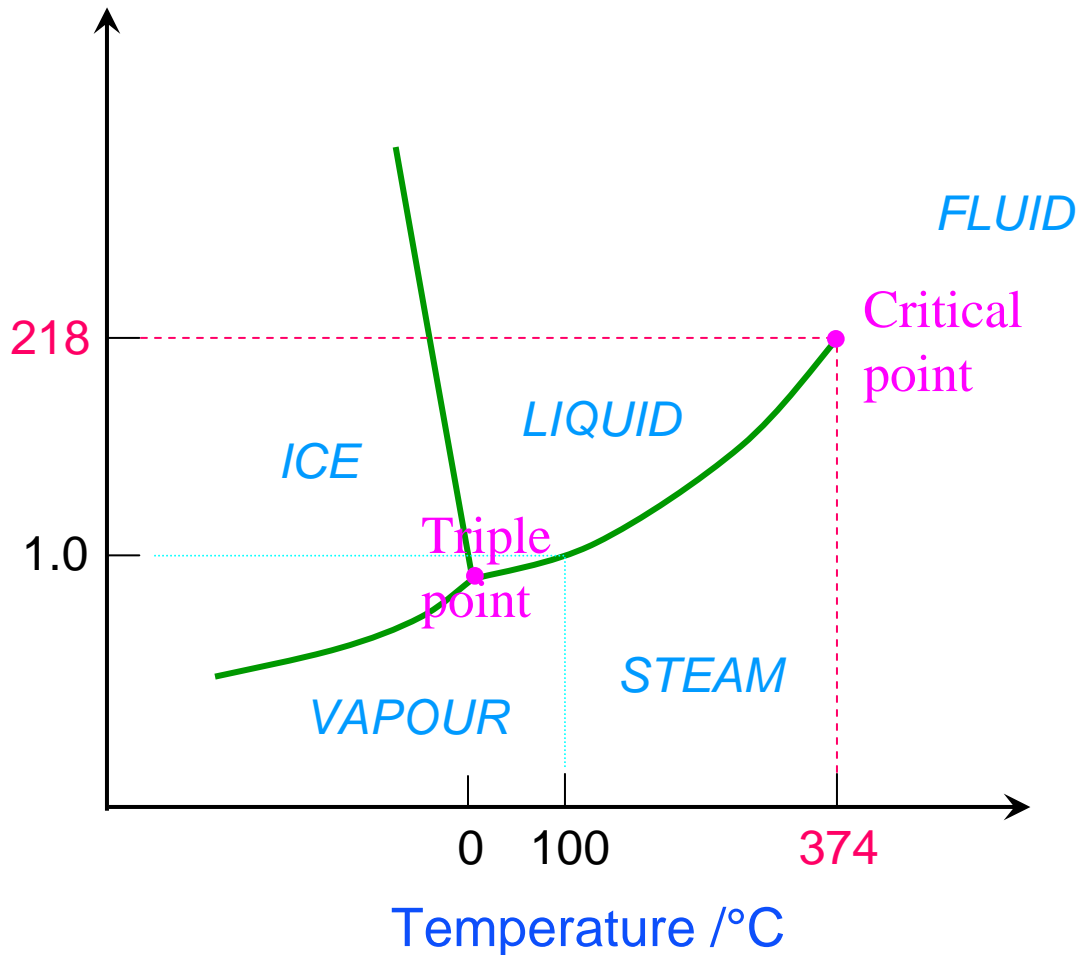
e.g. CO_2

Pressure



The Phase Diagram of Water

Pressure / atm



There are other solid phases at much higher pressures.